PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D04H 1/42, B01D 39/08, D01F 1/10 — A1

(11) International Publication Number: WO 97/07272

(43) International Publication Date: 27 February 1997 (27.02.97)

(21) International Application Number: PCT/US96/11878

(22) International Filing Date: 18 July 1996 (18.07.96)

(30) Priority Data:
08/514,866 14 August 1995 (14.08.95) US

(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

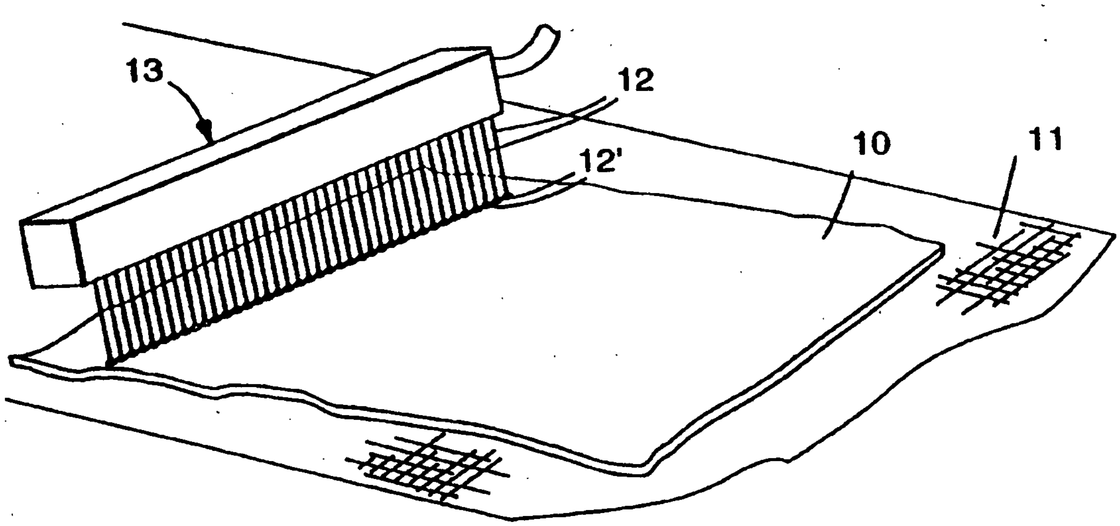
(72) Inventors: ROUSSEAU, Alan, D.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). JONES, Marvin, E.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). ANGADJIVAND, Seyed, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: HANSON, Karl, G. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: FIBROUS WEBS HAVING ENHANCED ELECTRET PROPERTIES



(57) Abstract

The present invention relates to a method of making a fibrous electret material which includes the steps of (1) forming a fibrous web of nonconductive thermoplastic fibers from a blend of nonconductive thermoplastic resin and an additive which is (a) a thermally stable organic compound or oligomer containing at least one perfluorinated moiety or (b) a thermally stable organic triazine compound or oligomer containing at least one nitrogen atom in addition to those in the triazine group or (c) a combination thereof; (2) impinging jets of water or a stream of water droplets onto the web at a pressure sufficient to provide the web with filtration enhancing electret charge; and (3) drying the web.

FIBROUS WEBS HAVING ENHANCED ELECTRET PROPERTIES

FIELD OF THE INVENTION

This invention provides fibrous webs capable of having enhanced electret properties, electret webs having such properties, compositions for preparing same, methods of preparing such webs and compositions and compounds useful in such webs and methods. The webs and compositions include blends of electret-forming polymers and electret property enhancing additives, the webs being charged by a process which includes impingement of jets of water or a stream of water droplets onto the web. The electret webs are particularly useful in filtration materials, for example for respirators or room or vehicle air filtration, and in other electrostatic aerosol filtration applications.

BACKGROUND OF THE INVENTION

For many years nonwoven fibrous webs have been used for filtration and other purposes. Some of such webs have been made from polypropylene using melt-blowing techniques of the type described in Report No. 4364 of the Naval Research Laboratories, published May 25, 1954, entitled "Manufacture of Super Fine Organic Fibers" by Van A. Wente et al. Such melt-blown microfiber webs continue to be in widespread use for filtering particulate contaminants, for example, as face masks and as water filters, and for other purposes, such as sorbent webs for removal of oil from water, as acoustic insulation and as thermal insulation.

The aerosol filtration efficiency of nonwoven fibrous webs can be improved by imparting an electrical charge to the fibers, forming an electret material. A number of methods are known for forming such electret materials. Such methods include, for example, bombarding melt-blown fibers as they issue from the die orifices, as the fibers are formed, with electrically charged particles such as electrons or ions, charging fibers by means of a corona discharge after fiber formation or imparting a charge to a fiber mat by means of carding and/or needle tacking (tribocharging). Recently, a method in which jets of water or a

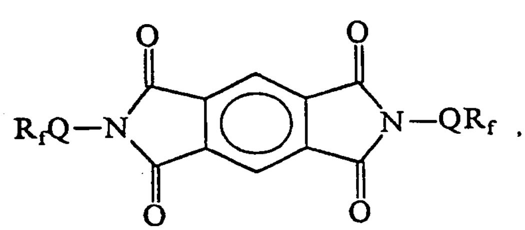
of silicone oil have been disclosed. The electret resin may optionally contain other additives, including heat stabilizers, weathering agents, anti-blocking agents, and inorganic or organic fillers. Charging may be carried out in various ways. Further disclosed are electret filter media with a melt processable fluorochemical additive having a melting point of at least 25°C and a molecular weight of about 500 to 2500. Charging involves subjecting the material to corona discharge or pulsed high voltage.

SUMMARY OF THE INVENTION

The present invention provides a method of making a fibrous electret material comprising the steps of (1) forming a fibrous web of nonconductive thermoplastic fibers from a blend of nonconductive thermoplastic resin and an additive which is (a) a thermally stable organic compound or oligomer containing at least one perfluorinated moiety, said compound or oligomer preferably having a fluorine content of at least about 18 percent by weight or (b) a thermally stable organic triazine compound or oligomer containing at least one nitrogen atom in addition to those in the triazine group or (c) a combination thereof; (2) impinging jets of water or a stream of water droplets onto the web at a pressure sufficient to provide the web with filtration enhancing electret charge; and (3) drying the web.

The present invention further provides a composition comprising a blend of a thermoplastic resin and at least one compound or oligomer which is

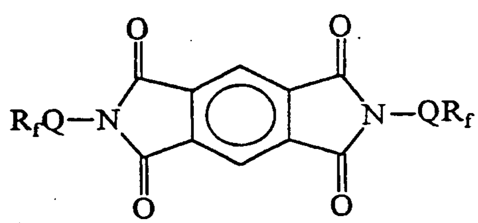
$$(R_fSO_2\underset{\displaystyle R}{\underset{|}{N}}CH_2CH_2O)_3P{=}O \ ,$$

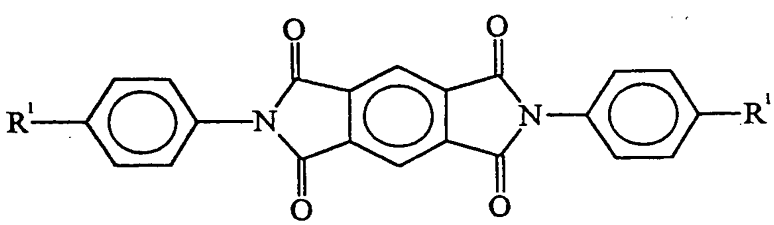


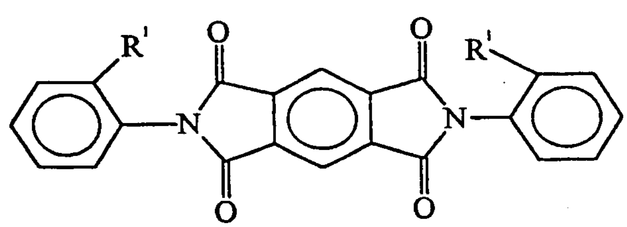
wherein R_f is a perfluorinated moiety preferably having about 3 to 20 carbon atoms, more preferably about 6 to 12 carbon atoms and which may contain one or more catenary ether oxygen atoms, Q is a linking group selected from alkylene groups having 1 or 2 carbon atoms, sulfonamido groups or combinations thereof, R is an alkyl group preferably having 1 to 4 carbon atoms, R^1 is a perfluoroalkyl group preferably having 1 to 4 carbon atoms, R^2 is an alkyl group which may be straight chain or branched and preferably having 4 to 10 carbon atoms and n is a number of from 2 to 40, preferably 2 to 20, more preferably 4 to 10.

The present invention, in another aspect, provides fibrous webs comprising a blend of a thermoplastic resin and at least one compound or oligomer which is

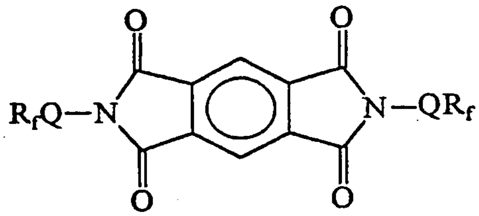
$$(R_fSO_2\underset{\displaystyle R}{\underset{|}{N}}CH_2CH_2O)_3P{=}O$$

 ,

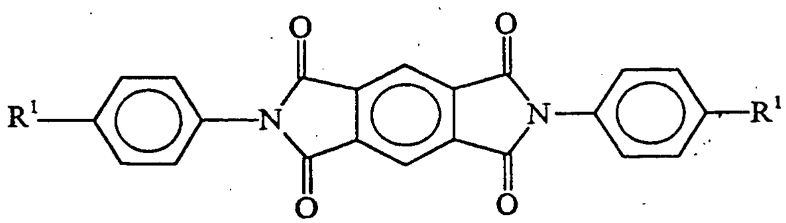
 ,

 ,

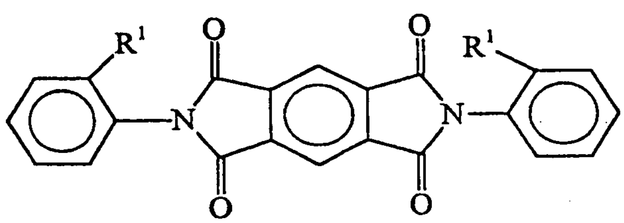
$$(R_fSO_2\underset{\substack{|\\R}}{N}CH_2CH_2O)_3P{=}O \quad ,$$



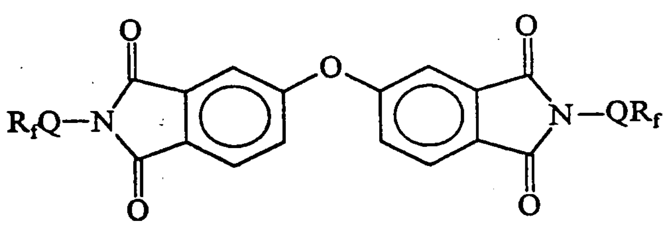
,



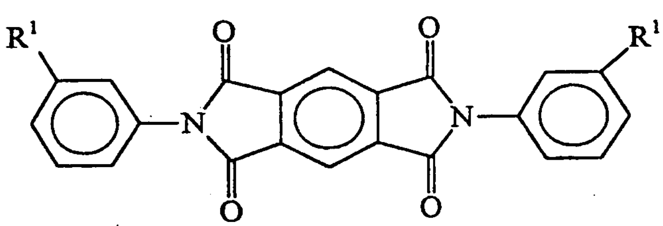
,



,



,



or

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side view of an apparatus useful in making the nonwoven microfiber web used in the method of the present invention.

FIG. 2 is a perspective view of a water jet spray apparatus useful in the present invention.

FIG. 3 is a perspective view of a nebulizer useful in the present invention.

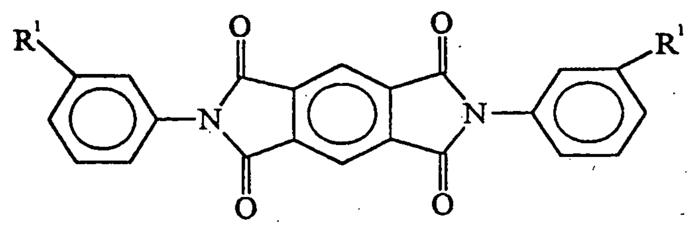
FIG. 4 is a perspective view of a pump action sprayer useful in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

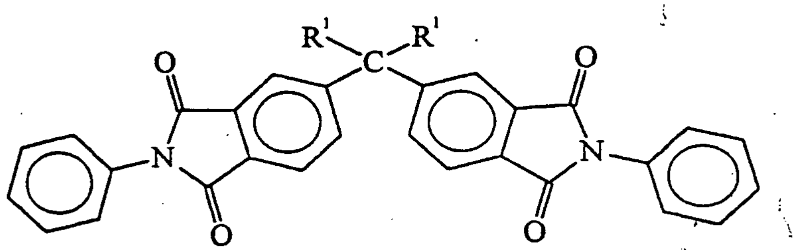
Thermoplastic resins useful in the present invention include any thermoplastic nonconductive polymer capable of having a high quantity of trapped charge when formed into a fibrous web treated by impingement of jets of water or a stream of water droplets. Polymers capable of acquiring a trapped charge include polyolefins such as polypropylene, polyethylene, and poly-4-methyl-1-pentene; polyvinyl chloride; polystyrene; polycarbonates; and polyesters. Preferred materials include polypropylene, poly-4-methyl-1-pentene, blends thereof or copolymers formed from at least one of propylene and 4-methyl-1-pentene.

One class of suitable additive materials is organic materials that contain at least one perfluorinated moiety and have a fluorine content of at least 18% by weight. These materials must be thermally stable at the extrusion temperature of the polymeric resin in order to withstand processing without undesirable degradation or volatilization. Usually molecular weights of 500 or greater are sufficient to avoid excessive volatilization. Such compounds include, for example, short-chain tetrafluoroethylene telomers, fluoroaliphatic alkanes having the formula C_xF_{2x+2} wherein x is from about 20 to 30,

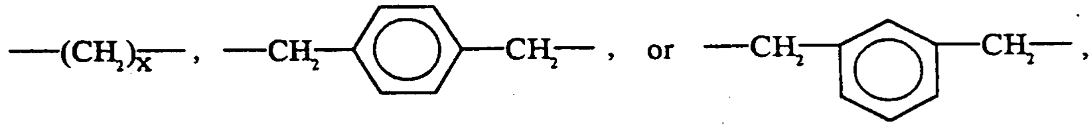
$$(R_fSO_2\underset{\substack{|\\ R}}{N}CH_2CH_2O)_3P{=}O \quad ,$$



or

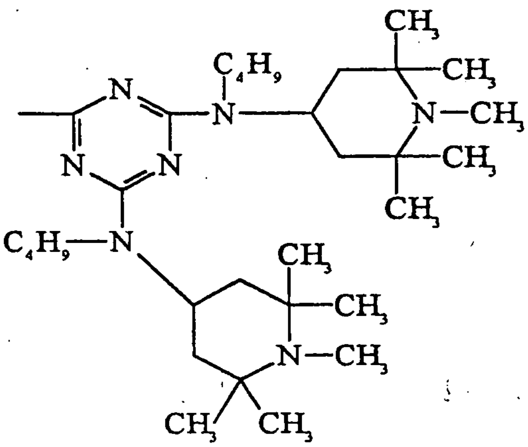


wherein R_f is a perfluorinated moiety preferably having about 3 to 20 carbon atoms, more preferably about 6 to 12 carbon atoms and which may contain one or more catenary ether oxygen atoms, Q is a linking group selected from alkylene groups having 1 or 2 carbon atoms, sulfonamido groups or combinations thereof, and R is an alkyl group preferably having 1 to 4 carbon atoms, R^1 is a perfluoroalkyl group preferably having 1 to 4 carbon atoms, and R^4 is



where x is 2 to 12.

Another class of suitable additive materials is organic triazine compounds or oligomers with at least one additional nitrogen-containing group. Again, they must be thermally stable at the extrusion temperature of the polymeric resin such that undesirable degradation or volatilization do not occur. Those compounds or oligomers having a molecular weight of usually at least 500 generally are not lost by volatilization. Such compounds or oligomers include

wherein R^3 is 

wherein R^2 is an alkyl group which may be straight chain or branched and preferably having 4 to 10 carbon atoms and n is a number of from 2 to 40, preferably 2 to 20, more preferably 4 to 10.

The fluorochemical additive or the triazine-based additive is preferably present in amounts of about 0.1 to 10 weight percent, more preferably about 0.2 to 5 weight percent, most preferably about 0.5 to 2 weight percent.

The blend of the thermoplastic resin and the additive can be prepared by well-known methods. The resin and the additive can be preblended and pelletized, then the pellets can be melt extruded. Alternatively, the additive can be blended with the resin in the extruder and then melt extruded. Useful extrusion conditions are generally those which are suitable for extruding the resin without the additive. The blended mixture may be processed into a fibrous filter web by any known technique.

Melt blown microfibers useful in the present invention can be prepared as described in Van A. Wente, "Superfine Thermoplastic Fibers," Industrial Engineering Chemistry, vol. 48, pp. 1342-1346 and in Report No. 4364 of the Naval Research Laboratories, published May 25, 1954, entitled "Manufacture of Super Fine Organic Fibers" by Van A. Wente et al.

The resin used to form the fibers useful in the present invention preferably is a thermoplastic nonconductive, i.e., having a resistivity greater than 10^{14} ohm·cm, resin capable of having a high quantity of trapped charge.

volume percent of the contents of the web. Such particle-loaded webs are described, for example, in U.S. Pat. No. 3,971,373 (Braun), U.S. Pat. No. 4,100,324 (Anderson) and U.S. Pat. No. 4,429,001 (Kolpin et al.), which are incorporated herein by reference.

The electret filter media prepared according to the method of the present invention preferably has a basis weight in the range of about 10 to 500 g/m^2, more preferably about 10 to 100 g/m^2. In making melt-blown microfiber webs, the basis weight can be controlled, for example, by changing either the collector speed or the die throughput. The thickness of the filter media is preferably about 0.25 to 20 mm, more preferably about 0.5 to 2 mm. The electret filter media and the resin from which it is produced should not be subjected to any unnecessary treatment which might increase its electrical conductivity, e.g., exposure to gamma rays, ultraviolet irradiation, pyrolysis, oxidation, etc.

Nonwoven microfiber webs useful in the present invention may be prepared using an apparatus as shown in FIG. 1. Such an apparatus includes a die 20 which has an extrusion chamber 21 through which liquified fiber-forming material is advanced; die orifices 22 arranged in line across the forward end of the die and through which the fiber-forming material is extruded; and cooperating gas orifices 23 through which a gas, typically heated air, is forced at high velocity. The high velocity gaseous stream draws out and attenuates the extruded fiber-forming material, whereupon the fiber-forming material solidifies as microfibers during travel to a collector 24 to form web 25.

When staple fibers are present in the web, they may be introduced through use of a lickerin roll 32 disposed above the microfiber blowing apparatus as shown in FIG. 1. A web 27 of staple fibers, typically a loose, nonwoven web such as prepared on a garnet or RANDO-WEBBER apparatus, is propelled along table 28 under drive roll 29 where the leading edge engages against the lickerin roll 32. The lickerin roll 32 picks off fibers from the leading edge of web 27 separating the fibers from one another. The picked fibers are conveyed in an air stream through an inclined trough or duct 30 and into the stream of blown microfibers where they become mixed with the blown microfibers. When particulate matter is to be

The enhanced performance of the filter media observed with the use of the fluorinated additives can often be yet further enhanced by annealing, i.e., heating for a sufficient time at a sufficient temperature to cause the fluorinated additive to bloom to the surface of the fibers. Generally, about 1 to 10 minutes at about 140°C is sufficient for polypropylene filter media although shorter times may be used at higher temperatures and longer times may be required at lower temperatures.

EXAMPLES

The following examples should not be construed as limiting in any way either the spirit or scope of the present invention. In the examples, all percentages and parts are by weight unless otherwise noted.

The following test method was used to evaluate the webs prepared in the examples:

DOP Penetration and Pressure Drop Test Method

Dioctyl phthalate (DOP) 0.3 micrometer diameter particles at a concentration of between 70 and 110 mg/m^3 are generated using a TSI No. 212 sprayer with four orifices and 30 psi (207 kPa) clean air. The particles are forced through a sample of filter media which is 11.45 cm in diameter at a rate of 42.5 L/min, which is a face velocity of 6.9 centimeters per second. The sample is exposed to the aerosol for 30 seconds. The penetration is measured with an optical scattering chamber, Percent Penetration Meter Model TPA-8F available from Air Techniques Inc. The pressure drop is measured at a flow rate of 42.5 L/min and a face velocity of 6.9 cm/sec using an electronic manometer.

The penetration and pressure drop are used to calculate a quality factor "QF" from the natural log (ln) of the DOP penetration by the following formula:

$$QF[1/\text{mm } H_2O] = \frac{-\ln\left[\dfrac{\text{DOP Penetration (\%)}}{100}\right]}{\text{Pressure Drop [mm } H_2O]}$$

A higher QF value indicates better filtration performance. Decreased QF values effectively correlate with decreased filtration performance.

from the manufacturer). The web had a basis weight of 52 g/m^2, an effective fiber diameter of 7.7 μm and a thickness of 0.9 mm.

Samples of the webs were subjected to impingement of water jets provided by a hydroentangler (Laboratory Model, serial no. 101, available from Honeycomb Systems Corp.), similar to that shown in FIG. 1, which had a spray bar width of 24 in (0.6 m) with 40 spray orifices, each 0.005 in (0.13 mm) in diameter, per inch (2.5 cm) width at a water pressure of 690 kPa. Each sample passed beneath the spray bar at a rate of 3.5 m/min, and was treated once on each face, vacuum extracted and dried at 70°C for one hour. The treated samples were tested for DOP penetration and pressure drop and the quality factor was calculated. The pressure drop and quality factor (QF) are reported in Table 1.

Table 1

	Pressure Drop (mm H_2O)	Quality Factor
Example 1	4.13	1.14
Comparative Example C1	2.73	1.01

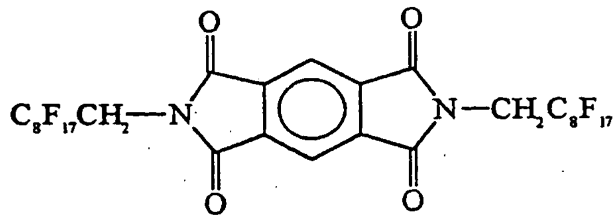
Example 2

Fluorotelomer (provided as VYDAX™, 20% dispersion of the telomer in trichlorotrifluoroethylene, available from E. I. Du Pont De Nemours & Co., Inc.) was isolated to yield a waxy short-chain telomer of tetrafluoroethylene with a molecular weight of about 3700 and a melting point of about 300°C.

Microfiber web was prepared and tested as in Example 1 except the fluorotelomer additive was used. The basis weight was 54 g/m^2, the effective fiber diameter was 6.2 μm, the thickness was 1.4 mm, the pressure drop was 4.06 and the quality factor was 1.18.

Example 3 and Comparative Example C3

Microfiber webs were prepared and tested as in Example 1 and Comparative Example C1 except the polypropylene used was ESCORENE PP-



For Examples 4 and 5 Comparative Examples C4 and C5, microfiber webs were prepared as in Example 1 and Comparative Example C1 except the polypropylene used was ESCORENE PP-3495G, available from Exxon Corp., the extrusion temperature was 240 to 260°C and the above-described additive was used. For Example 5 and Comparative Example C5, samples of the webs of Example 4 and Comparative Example C4 were annealed at 140°C for 10 minutes. The webs were tested for pressure drop and penetration and the quality factors were calculated. The pressure drop and quality factors are set forth in Table 3.

Table 3

	Basis Weight (g/m^2)	Effective Fiber Diameter (μm)	Thickness (mm)	Pressure Drop (mm H_2O)	Quality Factor
Example 4	49	8.1	1.1	1.68	0.63
Comparative Example C4	52	8.1	1.1	1.91	0.38
Example 5	49	8.1	1.1	1.83	0.82
Comparative Example C5	52	8.1	1.1	2.02	0.51

<u>Example 6-9 and Comparative Examples C6-C9</u>

A compound having the formula

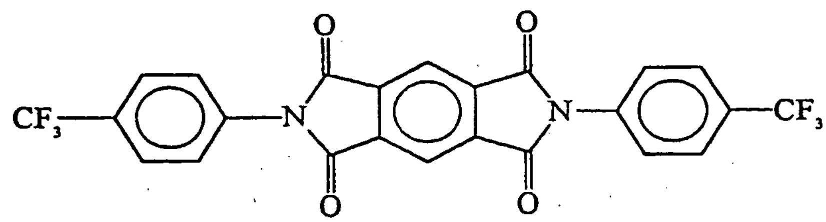
Table 4

	Basis Weight (g/m^2)	Effective Fiber Diameter (μm)	Thickness (mm)	Pressure Drop (mm H_2O)	Quality Factor
Example 6	54	8.9	1.1	1.86	0.66
Comparative Example C6	54	8.6	1.1	2.20	0.77
Example 7	54	8.9	1.1	1.90	1.39
Comparative Example C7	54	8.6	1.1	2.34	0.97
Example 8	54	8.4	0.9	2.05	0.51
Comparative Example C8	54	8.7	1.0	1.92	0.34
Example 9	54	8.4	0.9	2.21	1.10
Comparative Example C9	54	8.7	1.0	1.99	0.49

As can be seen from the data in Table 4, annealing the webs containing the additive significantly improved the filtration performance.

Examples 10 and 11 and Comparative Examples C10 and C 11

In Example 10, a web was prepared as in Example 1 using a perfluorinated alkane, $C_{24}F_{50}$,, available from Aldrich Chemical Co. as the additive. In Comparative Example C10, a similar web was prepared without additive. In Example 11 and Comparative Example C11, the webs of Example 10 and Comparative Example C10 were annealed as in Example 5. The basis weight, effective fiber diameter and thickness were determined for each web and are set forth in Table 5. The pressure drop and penetration were measured and the quality factor was determined. The pressure drop and quality factor are set forth in Table 5.



In Example 12, a web was prepared as in Example 1 using this additive. In Comparative Example C12, a similar web was prepared without additive. In Example 13 and Comparative Example C13, the webs of Example 12 and Comparative Example C12 were annealed as in Example 5. The basis weight, effective fiber diameter and thickness were determined for each web and are set forth in Table 6. The pressure drop and penetration were measured and the quality factor was determined. The pressure drop and quality factor are set forth in Table 6.

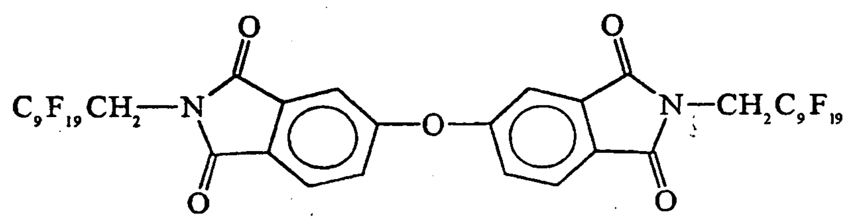
Table 6

	Basis Weight (g/m^2)	Effective Fiber Diameter (μm)	Thickness (mm)	Pressure Drop (mm H_2O)	Quality Factor
Example 12	54	8.3	1.1	1.98	1.01
Comparative Example C12	62	8.1	1.1	2.40	0.41
Example 13	54	8.3	1.1	2.03	1.25
Comparative Example C13	62	8.1	1.1	2.55	0.55

Example 14 and Comparative Example C14

To a stirred solution of 2-aminobenzotrifluoride (48.3 g, 0.30 mol) in 175 g N,N-dimethylformamide in a 1-liter flask at 65°C was added 1,2,4,5-benzenetetracarboxylic dianhydride (32.7 g 0.150 mol) over a period of two minutes. An exotherm to 85°C was observed and the solution was heated to 98°C

was cooled to 48°C and additional solid formed. To the stirred slurry were added 42 g acetic anhydride and 30 g pyridine and stirring was continued for about 4.5 hours. The slurry was then cooled to room temperature, filtered, and the isolated solid was washed with N,N-dimethylformamide and then methanol, and dried at 106°C to give 20.8 grams of a white solid additive having the structure.



Microfiber webs were prepared and tested as in Example 1 and Comparative Example C1 except the above-described additive was used. The results are set forth in Table 8.

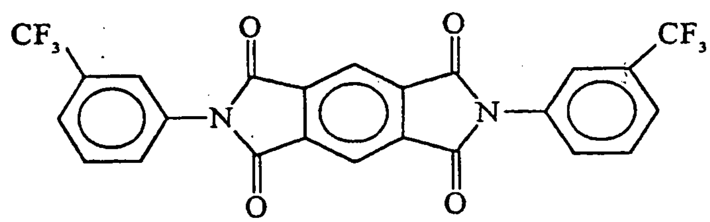
Table 8

	Basis Weight (g/m^2)	Effective Fiber Diameter (µm)	Thickness (mm)	Pressure Drop (mm H_2O)	Quality Factor
Example 15	54	7.3	1.0	2.62	0.87
Comparative Example C15	61	8.0	1.2	2.73	0.48

Example 16 and Comparative Example C16

To a stirred mixture of C_6F_{13} O $C_4F_8CH_2NH_2$ (30.0 g, 0.0531 mol, 73% pure) in 80 g N,N-dimethylformamide in a 250 mL flask at 63°C was added 4,4'-oxydiphthalic anhydride (6.17 g, 0.020 mol) over a period of five minutes. After heating for about 40 minutes a clear solution had formed. The solution was heated to 117°C and a small amount of an insoluble oil was removed and heating was continued for about 17.5 hours. The solution was cooled to 55° C, during which time solid had formed. Then, 35 g acetic anhydride and 25 g pyridine were

formamide. The solid was broken up and slurry which formed was stirred with mild heating for about three hours. After cooling to room temperature, the slurry was filtered and the filter cake was restirred in 350 g N,N-dimethylformamide, filtered a second time and washed with N,N-dimethylformamide and then methanol. The isolated solid was dried at 104°C to give 44.0 grams of pale-yellow solid additive which had the structure



Microfiber webs were prepared and tested as in Example 1 and Comparative Example C1 except the above-described additive was used. The results are set forth in Table 10.

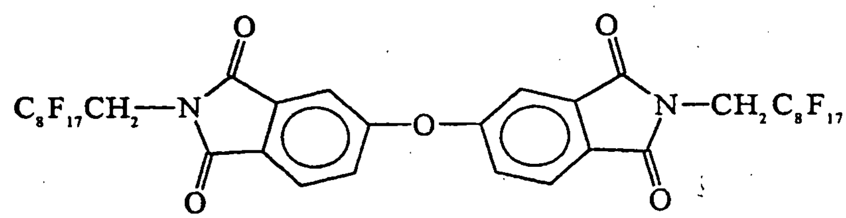
Table 10

	Basis Weight (g/m^2)	Effective Fiber Diameter (μm)	Thickness (mm)	Pressure Drop (mm H_2O)	Quality Factor
Example 17	54	7.8	1.2	2.11	0.75
Comparative Example C17	59	8.0	1.2	2.14	0.36

Example 18 and Comparative Example C18

To a stirred solution of aniline (16.8 g, 0.180 mol) in 150 g N,N-dimethylformamide in a 500 mL flask at 75°C was added 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (40.0 g, 0.090 mol) over a period of three minutes. An exotherm to 97°C was observed and the solution was heated to about 130°C for about 18 hours. After cooling to 67°C, 66 g of acetic anhydride and 44 g pyridine were added and heating was continued for about 3.5

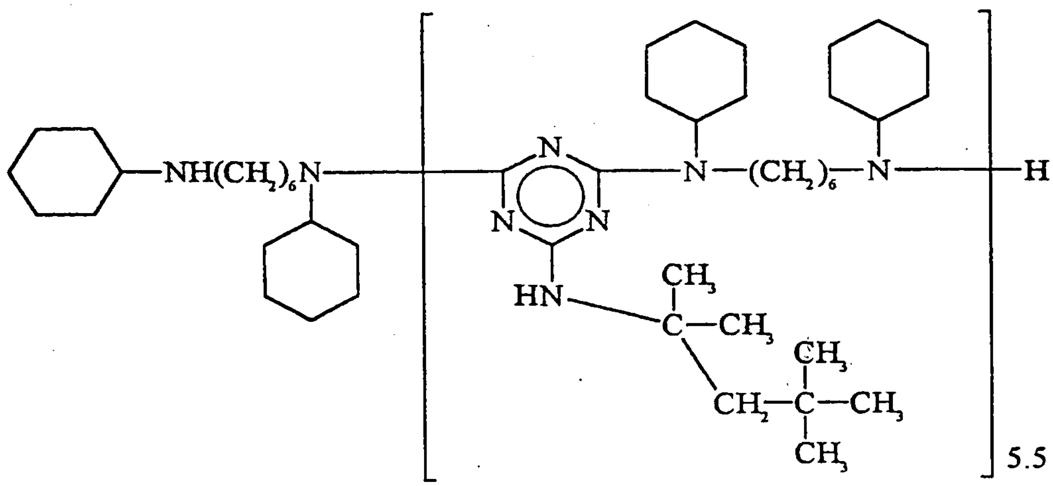
heating was continued for about 2.5 hours. After cooling to room temperature the slurry was filtered, washed with N,N-dimethylformamide, then methanol, and the isolated wet solid was dried at 104°C to give 22.6 g additive which had the structure



In Example 19, a web was prepared as in Example 1 except this additive was used , the polypropylene used was ESCORENE PP-3495G, available from Exxon Corp., and the extrusion temperature was 240 to 260°C. In Comparative Example C19, a similar web was prepared without additive. In Example 20 and Comparative Example C20, the webs of Example 19 and Comparative Example C19 were annealed as in Example 5. The basis weight, effective fiber diameter and thickness were determined for each web and are set forth in Table 12. The pressure drop and penetration were measured and the quality factor was determined. The pressure drop and quality factor are set forth in Table 12.

Table 12

	Basis Weight (g/m^2)	Effective Fiber Diameter (μm)	Thickness (mm)	Pressure Drop (mm H_2O)	Quality Factor
Example `19	49	8.0	1.1	1.87	0.92
Comparative Example C19	52	8.1	1.1	1.91	0.38
Example 20	49	8.0	1.1	1.99	0.80
Comparative Example C20	52	8.1	1.1	2.02	0.51



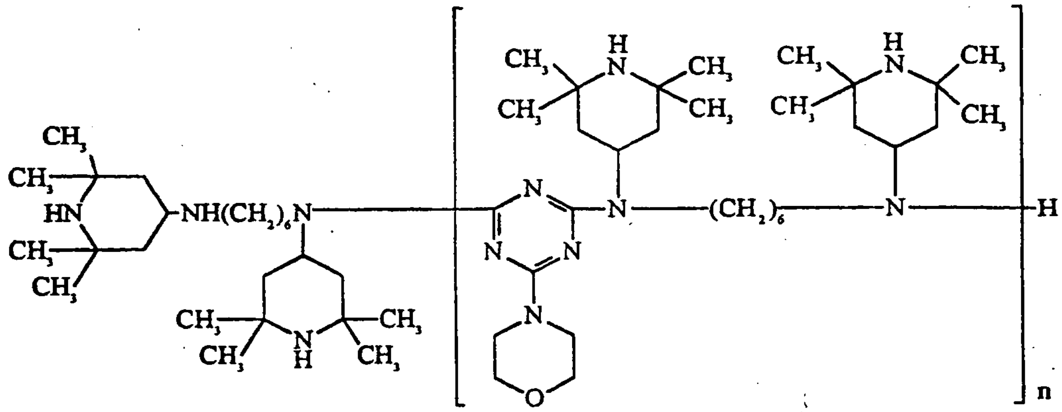
Microfiber webs were prepared and tested as in Example 1 and Comparative Example C1 except 0.5 weight percent additive was used in Example 22. The results are set forth in Table 14.

Table 14

	Basis Weight (g/m^2)	Effective Fiber Diameter (µm)	Thickness (mm)	Pressure Drop (mm H_2O)	Quality Factor
Example 22	57	8.5	1.1	2.26	1.04
Comparative Example C22	54	8.6	1.1	2.20	0.77

Example 23 and Comparative Example C23

A triazine product was prepared following the procedure of Example 22 except n-octylamine was used in place of tert.-octylamine in the preparation of the dichlorotriazine intermediate. The resulting additive had the structure



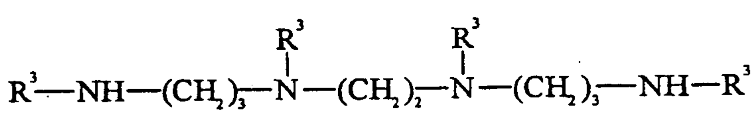
was used as the additive in Example 24. The results are set forth in Table 16.

Table 16

	Basis Weight (g/m^2)	Effective Fiber Diameter (μm)	Thickness (mm)	Pressure Drop (mm H_2O)	Quality Factor
Example 24	57	7.8	1.2	2.50	1.12
Comparative Example C24	56	7.0	1.3	2.53	0.46

Example 25 and Comparative Example C25

Microfiber webs were prepared and tested as in Example 1 and Comparative Example C1, except 0.5 weight percent CHIMASSORB™ 119, available from Ciba Geigy Corp. and having the structure



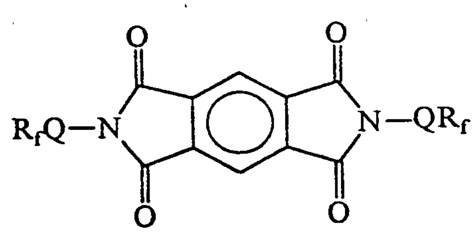
CLAIMS:

1. A method of making a fibrous electret material comprising the steps of (1) forming a fibrous web of nonconductive thermoplastic fibers from a blend of nonconductive thermoplastic resin and an additive which is (a) a thermally stable organic compound or oligomer containing at least one perfluorinated moiety or (b) a thermally stable organic triazine compound or oligomer containing at least one nitrogen atom in addition to those in the triazine group or (c) a combination thereof; (2) impinging jets of water or a stream of water droplets onto the web at a pressure sufficient to provide the web with filtration enhancing electret charge; and (3) drying the web.

2. The method of claim 1 wherein said thermoplastic resin is a polyolefin; polyvinyl chloride; polystyrene; polycarbonate; or polyester.

3. The method of claim 1 wherein said thermoplastic resin is polypropylene, poly-4-methyl-1-pentene, blends thereof or copolymers formed from at least one of propylene and 4-methyl-1-pentene.

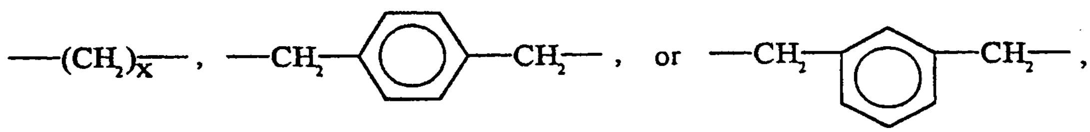
4. The method of claim 1 wherein said organic compound or oligomer containing at least one perfluorinated moiety is a short chain telomer of tetrafluoroethylene, fluoroaliphatic alkanes having the formula C_xF_{2x+2} wherein x is from about 20 to 30,



,

$$(R_fSO_2\underset{\substack{|\\ R}}{N}CH_2CH_2O)_3P{=}O \quad ,$$

wherein R_f is a perfluorinated moiety, Q is a linking group selected from alkylene groups having 1 or 2 carbon atoms, sulfonamido groups or combinations thereof, R is an alkyl group, R^1 is a perfluoroalkyl group, R^2 is an alkyl group which may be straight chain or branched, and R^4 is

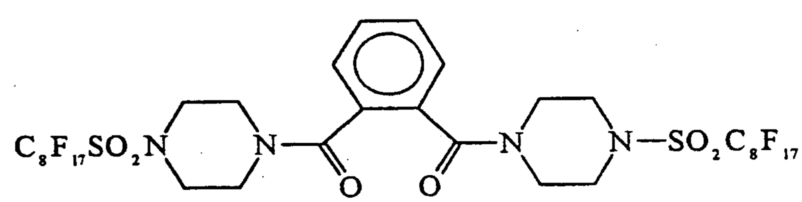


where x is 2 to 12, and n is a number of from 2 to 40.

5. The method of claim 1 wherein said compound or oligomer containing at least one perfluorinated moiety has a fluorine content of at least about 18 percent by weight.

6. The method of claim 1 wherein said organic compound or oligomer containing at least one perfluorinated moiety is a short-chain telomer of tetrafluoroethylene having a molecular weight of about 3700.

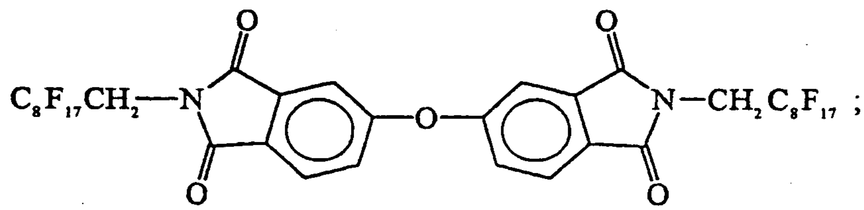
7. The method of claim 1 wherein said organic compound or oligomer containing at least one perfluorinated moiety is a compound represented by at least one of the following formulas:



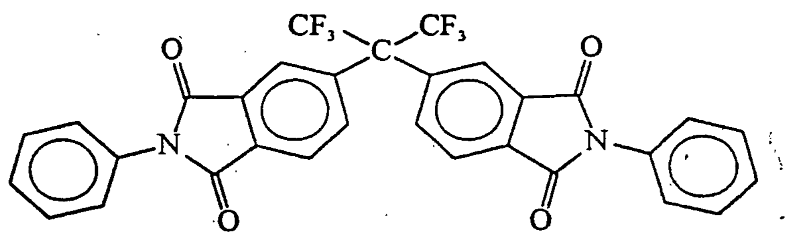
;

$$(C_8F_{17}SO_2\underset{\displaystyle C_2H_5}{\underset{|}{N}}CH_2CH_2O)_3P{=}O$$

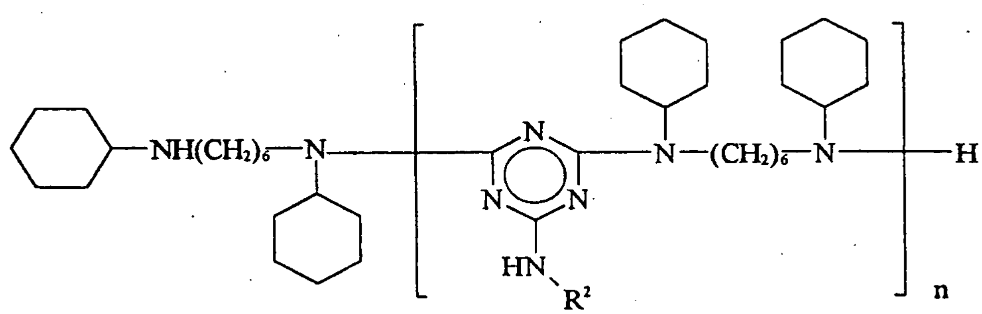
;

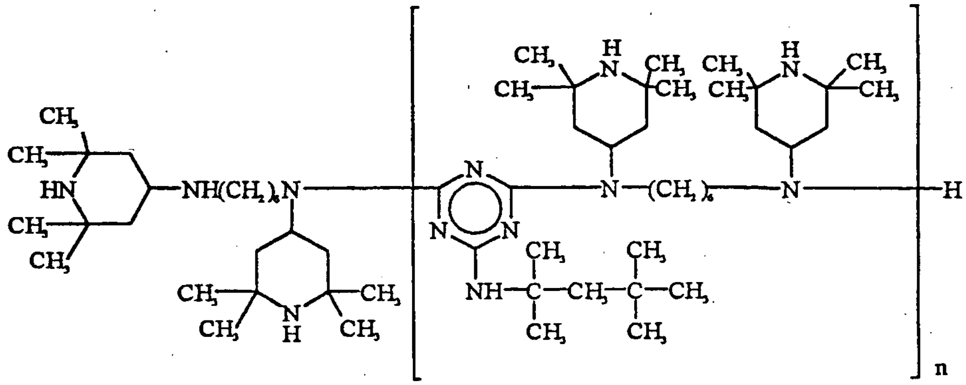


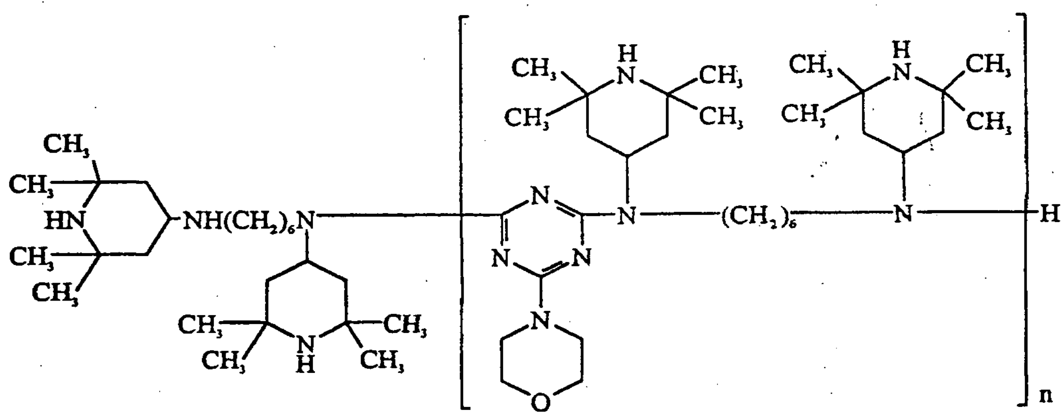
and



8. The method of claim 1 wherein said triazine compound is selected from the group consisting of:

(a) 

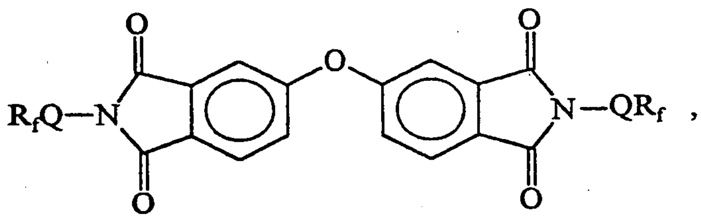


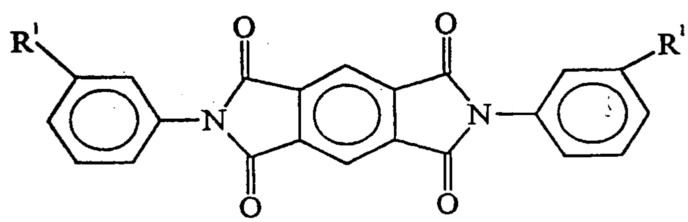


and

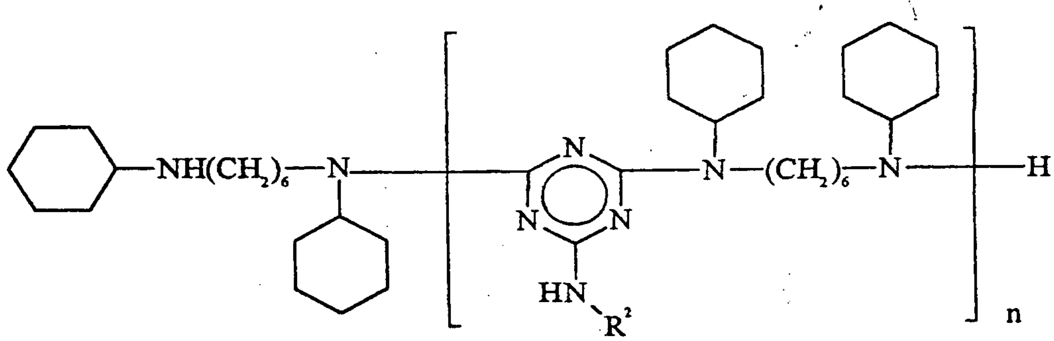
$$R^3-NH-(CH_2)_3-\underset{\displaystyle |}{\overset{R^3}{N}}\!\!-(CH_2)_2-\overset{R^3}{N}-(CH_2)_3-NH-R^3 \quad ;$$

wherein R^2 is an alkyl group and n is a number from 2 to 40; and





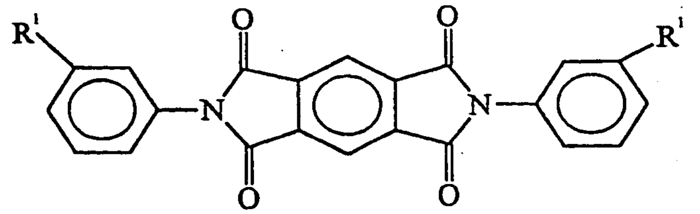
or



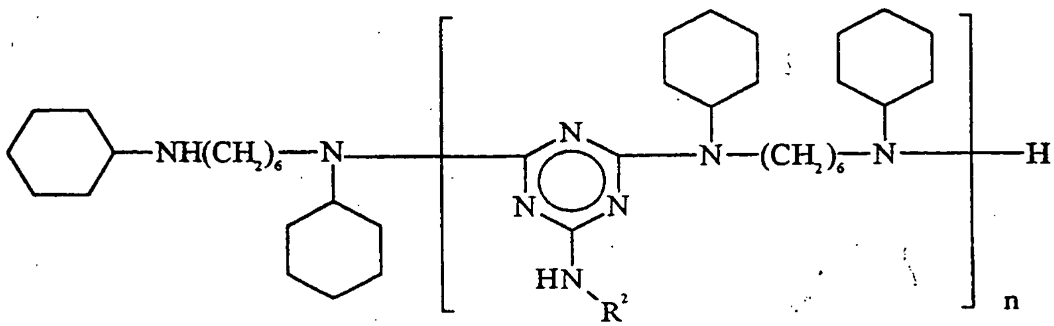
wherein R_f is a perfluorinated moiety which may contain one or more catenary ether oxygen atoms, Q is a linking group selected from alkylene groups having 1 or 2 carbon atoms, sulfonamido groups or combinations thereof, R is an alkyl group, R^1 is a perfluoroalkyl group, R^2 is an alkyl group that may be straight chain or branched and n is a number from 2 to 40.

10. The composition of claim 9 wherein said thermoplastic resin is a polyolefin, polyvinyl chloride, polystyrene, polycarbonate, or polyester.

11. The composition of claim 9 wherein said thermoplastic resin is polypropylene, poly-4-methyl-1-pentene, blends thereof or copolymers formed from at least one of propylene and 4-methyl-1-pentene.



or

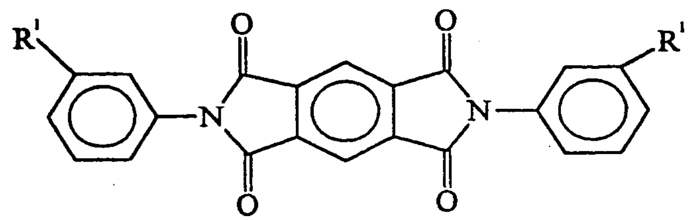


wherein R_f is a perfluorinated moiety which may contain one or more catenary ether oxygen atoms, Q is a linking group selected from alkylene groups having 1 or 2 carbon atoms, sulfonamido groups or combinations thereof, R is an alkyl group, R^1 is a perfluoroalkyl group, R^2 is an alkyl group which may be straight chain or branched and n is a number of from 2 to 40.

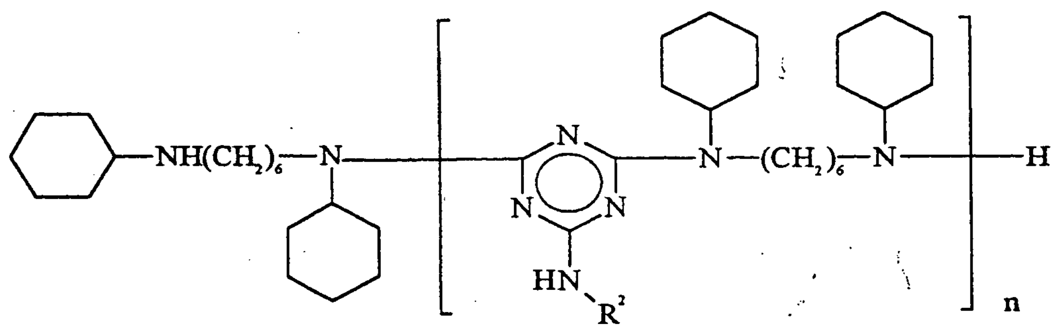
13. The fibrous web of claim 12 wherein said thermoplastic resin is a polyolefin, polyvinyl chloride, polystyrene, polycarbonate, or polyester.

14. The fibrous web of claim 12 wherein said thermoplastic resin is polypropylene, poly-4-methyl-1-pentene, blends thereof or copolymers formed from at least one of propylene and 4-methyl-1-pentene.

15. Electret filter media comprising a fibrous web of a blend of a thermoplastic resin and at least one compound or oligomer which is short-chain



or

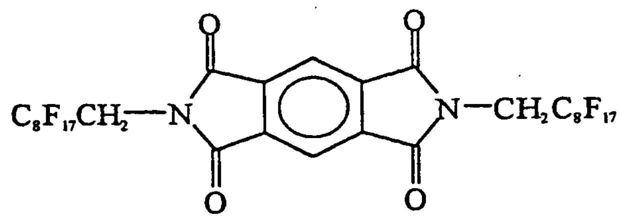


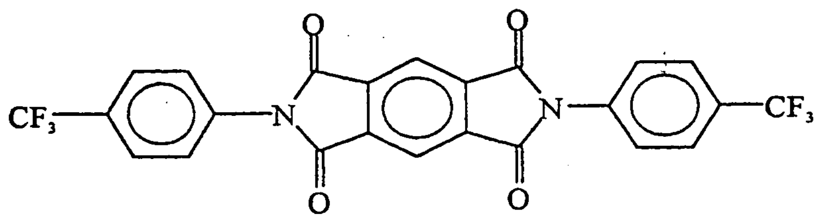
wherein R_f is a perfluorinated moiety which may contain one or more catenary ether oxygen atoms, Q is a linking group selected from alkylene groups having 1 or 2 carbon atoms, sulfonamido groups or combinations thereof, R is an alkyl group, R^1 is a perfluoroalkyl group, R^2 is an alkyl group which may be straight chain or branched and n is a number of from 2 to 40, said web having sufficient charge to exhibit improved filtration efficiency over a web having no compound or oligomer.

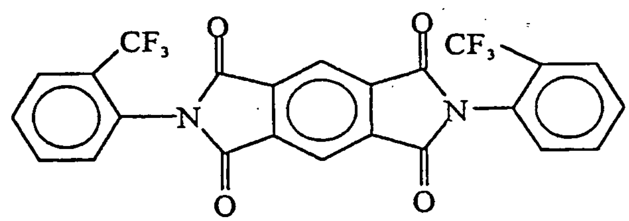
16. The electret filter media of claim 15 wherein said thermoplastic resin is a polyolefin, polyvinyl chloride, polystyrene, polycarbonate, or polyester.

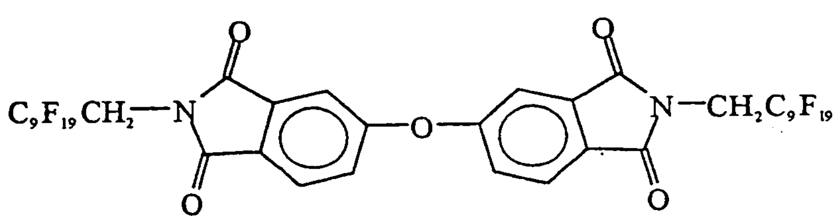
17. The electret filter media of claim 15 wherein said thermoplastic resin is polypropylene, poly-4-methyl-1-pentene, blends thereof or copolymers formed from at least one of propylene and 4-methyl-1-pentene.

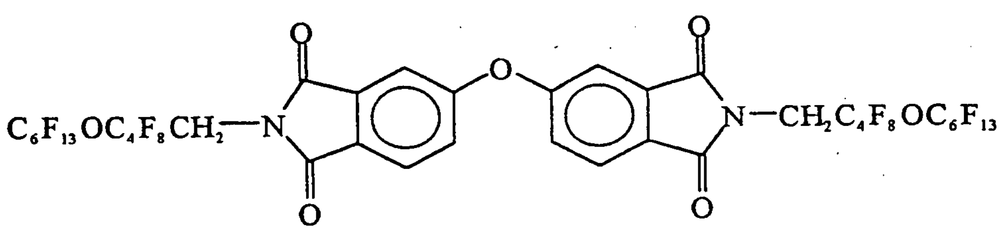
18. A compound selected from the group consisting of:

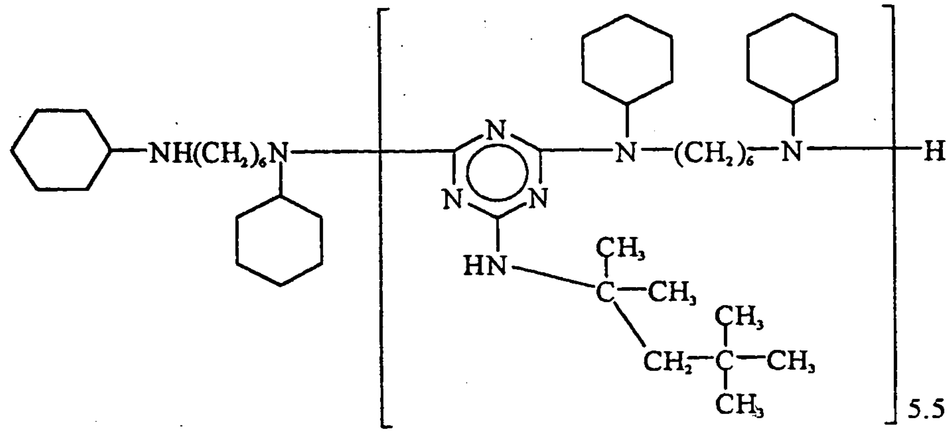
(6)  ,

(7)  ,

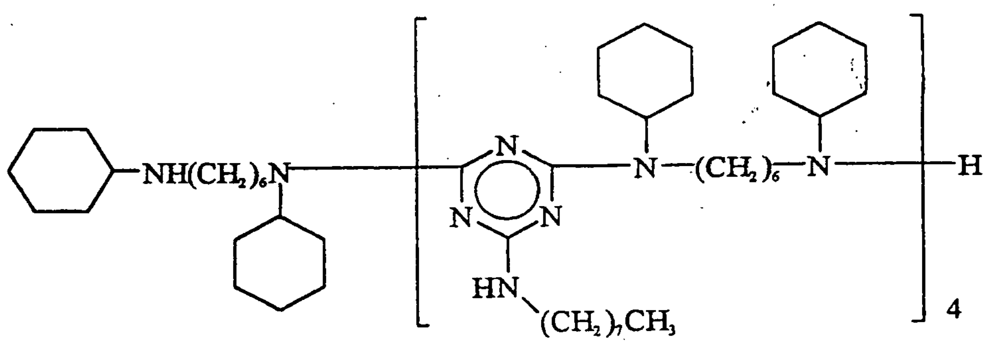
(8)  ,

(9)  ,

(10)  ,

(14) 

, and

(15) 

19. A respirator having a filtering means comprising the electret filter media of claim 15.

20. A vehicle ventilation system wherein the filtration means comprises the electret filter media of claim 15.

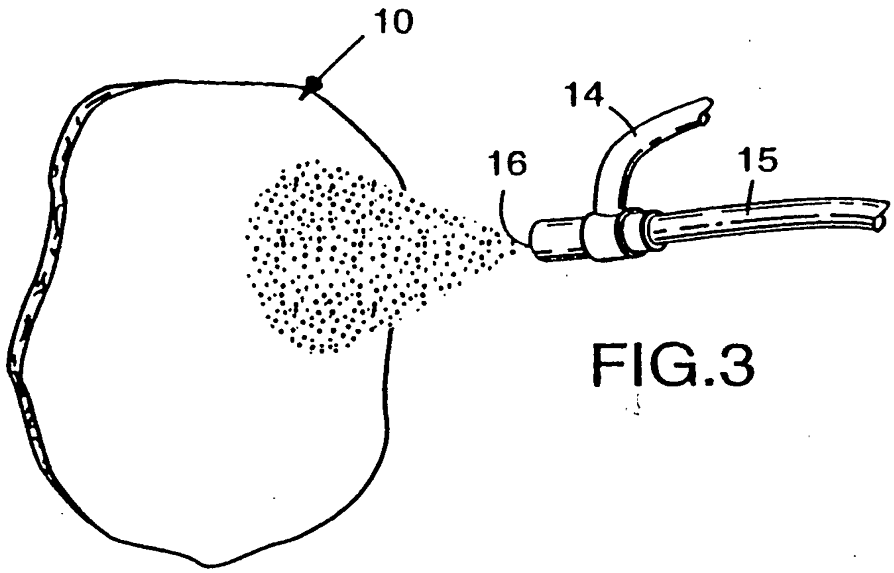


FIG.3

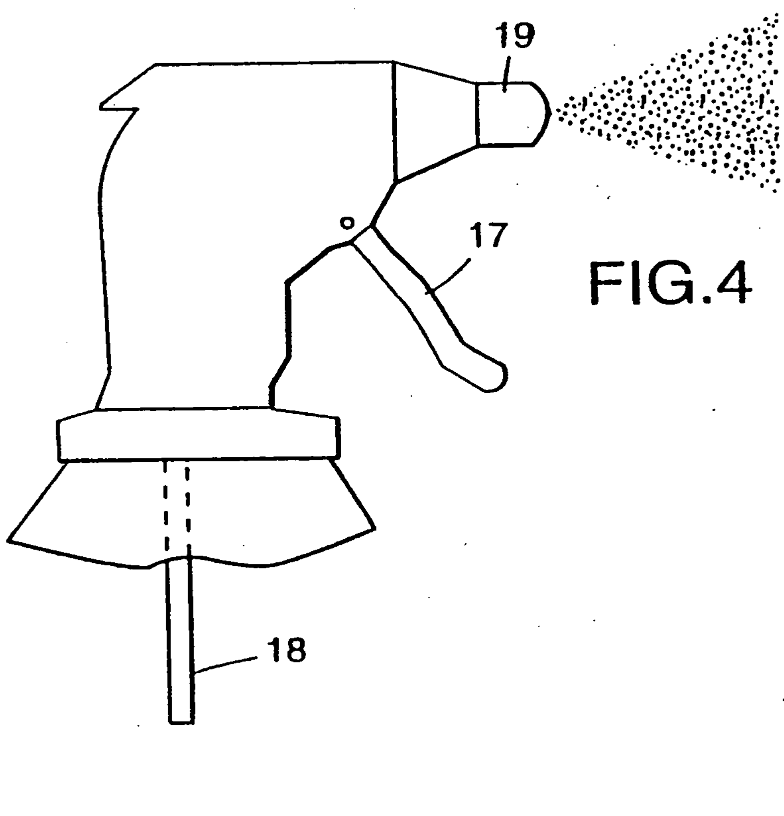


FIG.4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/11878

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,95 05501 (MINNESOTA MINING & MFG) 23 February 1995 see column 1, line 55 - column 4, line 9 ---	1-3
A	US,A,4 492 791 (ORBAN IVAN ET AL) 8 January 1985 cited in the application see the whole document -----	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/11878

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9505501	23-02-95	AU-A- 7953294	14-03-95
		BR-A- 9407259	24-09-96
		CN-A- 1129963	28-08-96
		EP-A- 0714463	05-06-96
		PL-A- 312993	27-05-96
		US-A- 5496507	05-03-96
US-A-4492791	08-01-85	CA-A- 1219870	31-03-87
		EP-A- 0093693	09-11-83
		JP-C- 1724404	24-12-92
		JP-B- 4004329	28-01-92
		JP-A- 58201820	24-11-83

Form PCT/ISA/210 (patent family annex) (July 1992)